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007 – SULFUR ISOTOPE COMPOSITIONS FROM DIFFERENT TYPE OF DEPOSITS IN THE BUCHIM-DAMJAN-BOROV DOL ORE DISTRICT, EASTERN MACEDONIA

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For, at least in part, determination of the origin of metals and sulfur in the ore district Buchim-Damjan-Borov Dol we made a series of complex research and analysis of the light isotope (^{32}S), heavy isotope (^{34}S), and their isotopic ratio ($\delta^{34}S$). In three deposits of the Buchim-Damjan-Borov ore district were sampled mostly pyrites from the hydrothermal range 250–350ºC (from each ore body mineral parageneses). For the porphyry copper ore deposits Buchim isotopic ratio values ranged from 0 to +2.09‰ averaging +0.982‰, while the Borov Dol values have shown wider range starting from –7.25 up to +0.72‰ averaging –2.238‰, due to enrichment with lighter sulfur isotope. Sulfur isotopic ratios for the Damjan Fe-skarn deposit have shown relative enrichment with heavy sulfur isotope resulting in value range of +1.75 up to +8.68‰ averaging +5.248‰.

Introduction

The Buchim-Damjan-Borov Dol ore district has been situated 15 km north-western from the city of Radoviš, Eastern Macedonia. This ore district is one of the most important in the country in regards of copper and iron deposits. Production of iron from the Fe-skarn deposit Damjan lasted from 1962 until 1992, the production of copper from the Buchim copper porphyry deposit started in 1979 and continues today as well, while the copper Borov Dol is at the stage of preparations for start of production. Sulfur isotope composition of sulfide minerals from the deposits in the Buchim-Damjan-Borov Dol ore district up to date have been studied by Serafimovski (1993), Serafimovski and Tasev (2005), etc. Analyses of sulfur isotope composition have been performed mainly on pyrite, rarely chalcopyrite and occasionally on galena (Borov Dol). This paper summarizes our latest findings concerning sulfur isotope composition of sulfide minerals from deposits in the aforementioned ore district.

Geological setting

The Buchim-Damjan-Borov Dol ore district has been defined as an individual metallogenic unit on the basis of the regional and local factors of metallogenetic control. Spatially, this ore district lies in two large geotectonic units (SMM and the Vardar zone), but metallogenetically it is part of the Lece-Chalkidiki metallogenetic zone (Serafimovski, 1993). The metallogeny of this ore district is directly related to the Tertiary intermediary calc-alkaline magmatism, which on today's erosion level has been

represented by subvolcanic-volcanic facies of andesite, latite, quartz-latite, trachyte, trachy-rhyolite, etc. The endogene mineralization of Fe, Cu, Au, Pb-Zn is related to this volcanogeno intrusive formation, genetically and spatially controlled by fault structures with NW-SE, NNW-SSE, NE-SW striking and at the places of their junctions and intersections. The endogene mineralization cycle in this area is related to the young Alpine metallogenetic epoch. Spatially, the deposits belong to two geotectonic blocks (the Buchim block and Damjan block), whereas genetically and paragenetically are related to the disjunctive structures and the Tertiary magmatism. The volcanic activity started by the end of Oligocene, while the ore mineralization took place during Miocene. Significant skarn type iron deposits, porphyry copper-gold deposits accompanied, locally, by hydrothermal vein type Pb-Zn, Ba mineralization, are dominant in this ore district. Generally,the ore mineralization was concentrated in three ore deposits: Buchim, Borov Dol (Cu-porphyry deposits) and Damjan (Fe-skarn deposit) .

Analytical methods

Within this study were analyzed pyrite, chalcopyrite and galena samples from the Buchim, Borov Dol and pyrites from the Damjan deposit (34 samples in total). The analyses were performed at the analytical facilities of the Geology Department at the Royal Holloway, University of London. The Fisons Instruments "Isochrom-EA" system used here consists of an elemental analyzer (EA1500 series 2), on line to an Optima mass spectrometer operating in continuous flow mode (Grassineau et al., 2001). Measured sulfur contents are within 1–1.5% of expected values and the reproducibility of $\delta^{34}S$ values is (0.1‰ (1σ).

Results and Discussion

Three ore were subject for study of sulfur isotope ratios in major sulfide minerals within the Buchim-Damjan-Borov Dol ore district. Two of them are Cu-porphyry copper deposits (Buchim and Borov Dol) while the third one is Fe-skarn deposit (Damjan) that is localized on the central parts of the district. The results and discussion are shown separately for each deposit. The Figure 1 shows the variation diagram of the isotopic composition of sulfur ($\delta^{34}S$) in individual deposits in the Republic of Macedonia and the southwestern parts of North America (Cooke, 1983; Anderson et al., 2001) and as can be seen, Buchim and Borov Dol porphyry Cu-deposits show quite compatible range with for example Mariquita deposit (Salas et al., 2013). Also, the Damjan Fe-skarn deposit sulfur isotope ratios does not differ much from similar deposits elsewhere, Nifty (Cooke, 1983). According to the histogram illustration and comparative graphic analysis shown at Figure 1 it can be concluded that all of the three deposits from the Buchim-Damjan-Borov Dol ore district show sulfur isotope ratio values within range –7.58 – +8.68‰, which confirms that sulfur in studied minerals is of endogene origin and does not exceeds limit values of –10 – +10‰ (Ohmoto and Rye, 1979; Shimazaki and Sakai, 1984). Data show that sulfur, and probably the ore metals

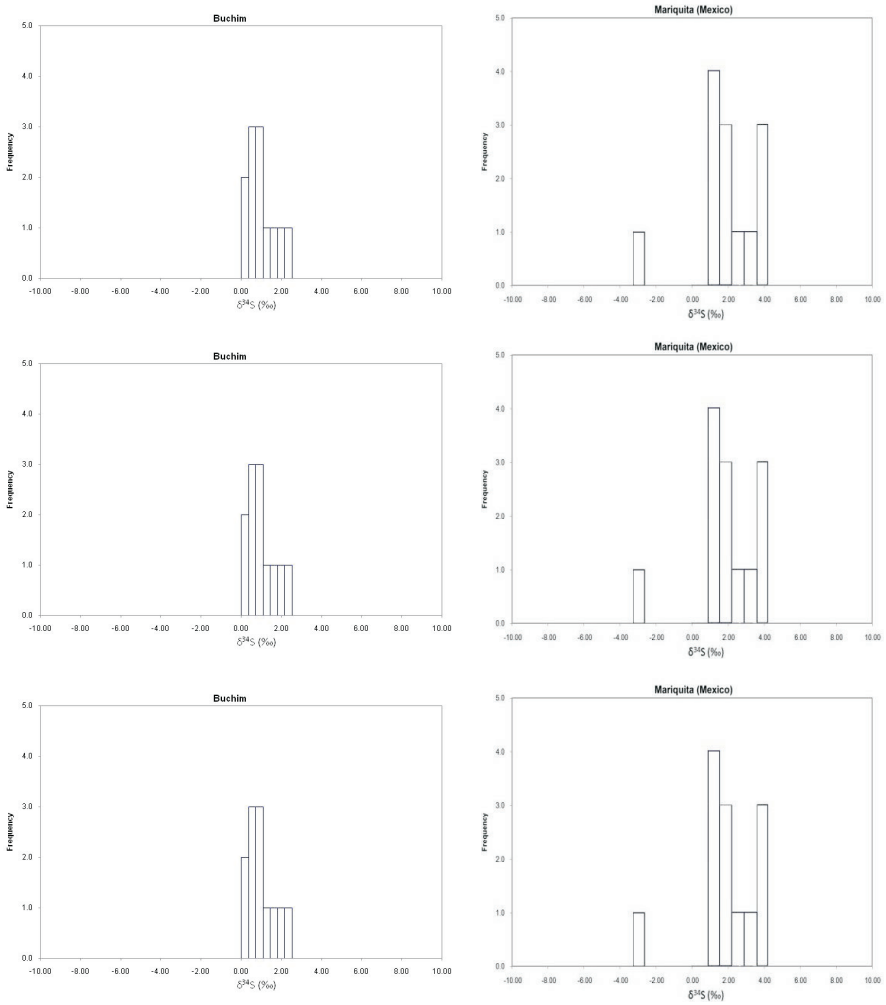

Figure 1. Histograms of distribution frequency for $\delta^{34}S$ in the studied and compared deposits a) Buchim porphyry copper deposit; b) Borov Dol porphyry copper deposit; c) Damjan Fe-skarn deposit; d) Mariquita porhyry copper deposit and e) Nifty Cu-skarn deposit

in the deposit as well, are of primary origin and sulfur sources are related to the deep parts of the Earth's crust or the bordering area between the continental crust and the upper mantle. The range of $\delta^{34}S$ values is close to values characteristic for magmatic sulfur, 0‰ ± 5‰ $\delta^{34}S$ (Field and Gustafson 1976; Ohmoto and Rye 1979; Shelton and Rye 1982; Weihed and Fallick 1994). However we do not want to overlook fact that magmatic fluids assimilated one small fraction of sulfur from adjacent rocks (Ohmoto and Goldhaber, 1997). Determined range of $\delta^{34}S$ values in sulfide minerals from the

Buchim and Borov Dol deposits is representative for ore-bearing parts in granitic composition rocks, as it was mentioned elsewhere (Douglas et al., 2003) and porphyry Cu ± Mo deposits.

Bearing in mind that the majority of sulfur isotope ratios for the Buchim and Borov Dol ranged –3.02 to +2.53‰, indicates that the source of sulfur for both deposits is clearly magmatic (Salas et al., 2013). Sulfur deposited at high temperatures should show less fractionation between minerals than that deposited at low temperatures (Brownlow, 1996). However, it is possible that one small fraction, of slightly increased positive values of $\delta^{34}S$ in particular parts of the studied area are due to increased influence of sulfur from meteoritic waters (Bi et al., 2004; Ohmoto and Rye, 1979). This is especially accented in oxidation and secondary enrichment zones where due to direct connection of meteoritic waters with magmatic ones resulted in sulfur fractionation and occurred enrichment of heavy S isotope. However, narrow range of values and local presence of pyrrhotite suggests homogenous source and reduction ore-bearing fluid with sulfide domination that corresponds with claims of Ohmoto and Rye (1979).

The most consistent values of sulfur isotope ratios has been determined in studied minerals from the Buchim deposit (+0.16 – 2.53‰ $\delta^{34}S$), which beside other factors probably is due to movement of ore-bearing fluids through the homogeneous stratigraphic sequences of the Serbo-Macedonian mass' crystalline.

For the Borov Dol Cu-porphyry deposit has been evident existence of sulfur fractionation and enrichment with lighter sulfur isotope (–7.52 to +0.72‰ $\delta^{34}S$), especially within galena that in the particular mineral assemblage came the latest at temperatures lower than 200ºC.

The Damjan Fe-skarn deposit has been characterized by relatively increased positive values of $\delta^{34}S$ (+1.75 to +8.68, Table 3, Fig. 2), which points out to sulfur fractionation and subsequent enrichment with heavier sulfur isotope. According to ours aforementioned explanation, beside that the ore-bearing solutions passed through the different lithological units (marls, limestone, clays, skarns etc.), here once again we would like to point out that sulfur isotope composition has been studied in pyrites from the latest stage of the ore-bearing process (Serafimovski, 1982). They are morphologically almost ideal (typical hexahedra), very large (2–3 cm) and exhibit zonal internal composition, which points out to the fact that they have crystallized from gel mixtures at far lower temperatures compared to the major iron ore minerals in the Damjan deposit, magnetite and hematite (Zarić, 1977).

Conclusion

The studies of sulfur isotope composition, in three copper and iron deposits of porphyry and skarn genetic type in the Republic of Macedonia, have shown that the narrowest range of sulfur stable isotope values were determined with study of ore samples from the Buchim Cu-porphyry deposit (+0.16 – 2.53‰ $\delta^{34}S$), which coincides with

values determined in similar deposits elsewhere in the World. Studies of sulfur stable isotope ratio ranging –7.52 – 0.72‰ $\delta^{34}S$ in Borov Dol Cu-porphyry deposit have shown emphasized sulfur fractionation and change of its primary composition followed by enrichment with lighter sulfur, as a result of lithostratigraphic setting (ophiolite melange, Creataceous sediments, volcanic rocks) where have passed ore-bearing fluids. The sulfur isotope composition in the Damjan Fe-skarn deposit varies from +4.02 up to to +8.68‰ and shows tendency of fractionation and enrichment with heavier sulfur, which is similar to data shown elsewhere (Shimazaki and Sakai, 1984). To the change of primary sulfur contributed ore deposition setting (carbonates, skarns, flysch sediments) as well as deposition of coarse grained pyrites during the later low-temperature mineralization stage.

References

1. Anderson, R.B., Gemmell, J.B. and Berry, F.R. 2001. The Geology of the Nifty Copper Deposit, Throssell Group, Western Australia: Implications for Ore Genesis. Economic Geology, 96, pp. 1535–1565.
2. Bi, X., Hu, R. and Cornell, D.H. 2004. The alkaline porhyry associated Yao'an gold deposit, Yunnan, China: rare earth element and stable isotope evidence for magmatic-hydrothermal ore formation. Mineralium Deposita, 39, pp. 21–30.
3. Cooke, J.B. 1983. Geology, mineral equilibria, sulfur, rubidium-strontium and lead isotopes and intrusion chemistry of the McDame tungsten skarn prospect, North Central British Columbia. Master thesis, The Universityof British Columbia Dept. Geol. Sci., 63 pp.
4. Douglas, T.A., Chamberlain, C.P., Poage, M.A., Abruzzese, M., Shultz, S., Henneberry, J. and Layer, P. 2003. Fluid flow and the Heart Mountain fault: A stable isotopic, fluid inclusion, and geochronologic study. Geofluids 3(1), pp. 13–32.
5. Field, C.W. and Gustafson, L.B., 1976. Sulfur isotopes in the porphyry copper deposit at El Salvador, Chile. Econ. Geol. 71, pp. 1533–1548.
6. Grassineau, V.N., Mattey, P.D. and Lowry, D., 2001. Sulfur Isotope analysis of sulfide and sulfate minerals by continuous flow-isotope ratio mass spectrometry. Analytical Chemistry, 73(2), pp. 220–225.
7. Ohmoto, H. and Goldhaber, B.M. 1997. Sulfur and carbon isotopes. In: Geochemistry of hydrothermal ore deposits. Ed. Hubert Lloyd Barnes, 3rd edn. Wiley & Sons, Inc., 972 pp.
8. Ohmoto, H. and Rye, R.O. 1979. Isotopes of sulfur and carbon. In: Geochemistry of hydrothermal ore deposits, Ed. H.L. Barnes, 2nd edn. Wiley & Sons, Inc., pp. 509–567.
9. Salas, R.D.R, Ochoa-Landín, L., Ruiz, J., Eastoe, C., Meza-Figueroa, D., Zuñiga-Hernández, H., Mendívil-Quijada, H. and Quintanar-Ruiz, F. 2013. Geology, stable isotope, and U-Pb geochronology of the Mariquita porphyry copper and Lucy Cu-Mo deposits, Cananea District, Mexico: A contribution to regional exploration. Journal of Geochemical Exploration, 124, 2013, pp. 140–154.
10. Serafimovski,T.1982: Metalogenetske karakteristike skarnovskog Fe-lezista Damjan. Magistarska teza, RGF-Beograd, Beograd.
11. Serafimovski, T.1993: Structural-metallogenetic Features of the Lece-Chakidiki Zone: Types of Mineral Deposits and Distribution. Faculty of Mining and Geology, Geological Department, Special Issue No. 2, p. 328, Stip.
12. Serafimovski, T. and Tasev, G. 2005: Sulfur isotope composition of some polymetalic deposits in the Republic of Macedonia. Geologica Macedonica, Stip, 19, pp. 1–11.

13. Shelton, K.L. and Rye, D.M. 1982. Sulfur isotope compositions of ore from Mines Gaspe, Quebec: An example of sulfate-sulfide isotopic disequilibria in ore-forming fluids with applications to other porphyry-type deposits. Economic Geology, 77, pp. 1688–1709.
14. Shimazaki, H. and Sakai, H. 1984. Regional Variation of Sulfur Isotopic Composition of Skarn Deposits in the Westernmost Part ofthe Inner Zone of Southwest Japan. Mining Geology, 34(6), pp. 419–424.
15. Weihed, P. and Fallick, A.E. 1994. A stable isotope study of the Palaeoproterozoic Tallberg porphyry-type deposit, northern Sweden. Mineralium Deposita, 29(2), pp. 128–138.
16. Zarić, P. 1977. Typomorph metallogenetic features of magnetites in Yugoslavia. Doctoral thesis, Faculty of Mining and Geology, Belgrade, 287 pp. (in Serbian)

008 – LEAD ISOTOPES AS TRACER FOR LAND USE POLLUTION IN SOILS AND SEDIMENTS OF TWO DIFFERENT WATERSHEDS

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Lebanon shows an important advancement in both agricultural and industrial sectors during the last 30 years. However, the untreated wastes from industrial and agricultural practices are rejected to the terrestrial and aquatic environment. The waste of the 288 local industries along the Litani basin and the fertilizer factory on the Levantine basin are enriched by Pb, thus we chose stable Pb isotopes to originate pollution source and detect contamination level in this geochemical research due to its precision and specificity. Stable Pb isotopic ratios ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb in two different watersheds in Lebanon were analyzed for soil and sediments. Samples were collected from both costal industrial area and inland agricultural water catchments. In the industrial area, data show a clear mixing line between 2 sources: natural bed rock and contaminated fuel and aerosol, by which samples in the vicinity of the factory are more contaminated [1, 2]. The high Pb^{206}/Pb^{207} ratio (mean ratio of the costal marine sediment is 1.81) is due to the fact that Pb is a daughter element of decayed uranium [3], which is originated from apatite rocks used as row material in the manufacturing process. Pb Isotopic ratios in the agricultural area vary in the sediments collected from the reservoir spatially and seasonally, by which it divides the reservoir into 3 zones (river inlet, central and dam zone). We observe a clear mixing line between sediments in the reservoir by which river inlet brought more anthropogenic contaminated sediments and the first flush wash out the dissolved solids from the upper basin. Particulate Ca